Hydrothermal Synthesis, Crystal Structure and Catalytic Properties of a Novel Polyoxometalate: $(C_5H_7N_2)_3(AsMo_{12}O_{40})\cdot 2C_5H_6N_2\cdot 1.5H_2O$

Tie-Jun Cai, Xiao-Ming Shen, Zhen-Shan Peng, Shu-Zi Lü, and Qian Deng

Key Laboratory of Theoretical Chemistry and Molecular Simulation of Ministry of Education,
Hunan University of Science and Technology, Xiangtan 411201, China

Reprint requests to Prof. Tie-Jun Cai. Fax: +86-731-58291379. E-mail: tjcai53@163.com

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$(C_5H_7N_2)_3(AsMo_{12}O_{40})\cdot 2C_5H_6N_2\cdot 1.5H_2O$ was hydrothermally synthesized and structurally characterized by single-crystal X-ray diffraction. Crystal data: monoclinic, $P2_1/n$, a = 13.310(3), b = 22.399(5), c = 19.820(4) Å, β = 99.99(3) °, V = 5819(2) Å^3, Z = 1, $wR(F^2)$ = 0.1345. The structure consists of Keggin-type $[AsMo_{12}O_{40}]^{3-}$ polyoxoanions. The title compound has a high catalytic activity for the oxidation of acetone tested in a continuous-flow fixed-bed micro-reactor. When the initial concentration is 5.3 g m^{-3} in air and the flow rate is 2.5 mL min^{-1}, the acetone is completely eliminated at 150 °C.

Key words: Polyoxometalate, Hydrothermal Synthesis, Keggin Structure, Crystal Structure, Catalytic Elimination

Introduction

Polyoxometalates (POMs) have attracted considerable attention owing to their various properties and potential applications in chemistry, medicine, catalysis, electronics, and magnetism [1 – 3]. In particular, the study on functionalization of POMs has become a significant direction to develop new inorganic-organic hybrid materials with useful properties. Therefore, much effort has been devoted to finding effective linkers for POM building units in order to form novel structures for potential applications. To date, many inorganic-organic hybrid materials, including transition metal phosphates [4, 5] and vanadium, molybdenum oxides [6], phosphatomolybdate or arsenomolybdate charge-transfer complexes [7 – 11] have been synthesized. More recently, Zhang [12] and Soumahoro [13] have reported molybdenum-arsenate polyoxometalates synthesized under hydrothermal conditions. However, studies on arsenomolybdate-2-aminopyridine polyoxometalates are scarce. We were interested in exploring the arsenomolybdate Keggin-type POMs to find new hybrid compounds.

Acetone is an important industrial raw material and a typical small molecule organic pollutant. The Chinese Industrial Standard TJ 36-79 [14] states that the maximum allowable concentration of acetone is 0.4 g m^{-3} in a working zone atmosphere. Thus the elimination of acetone has an environmental significance. In this paper, we report a new arsenomolybdate, $(C_5H_7N_2)_3(AsMo_{12}O_{40})\cdot 2C_5H_6N_2\cdot 1.5H_2O$ (**1**), synthesized by the hydrothermal method. The oxidative elimination of acetone from air was used as a probe reaction to evaluate the catalytic activity of the new hybrid compound.

Experimental Section

Elemental analyses were performed using a Perkin–Elmer 2400 CHNS/O analyzer. The contents of Mo and As were determined by a Shimadzu ICPS-7510 instrument. The infrared spectrum was recorded from KBr pellets (4000 – 400cm^{-1}) on a Perkin–Elmer FTIR-2000 spectrophotometer. UV/Vis spectra were recorded on a Perkin-Elmer Lambda-35 spectrophotometer in water. Thermal analysis (TG-DTA) was carried out on a WCT-1D differential thermal balance (Beijing Optical Instrument Factory, China) in air atmosphere with a heating rate of 10 °C min^{-1}.

Hydrothermal synthesis

All chemicals of p. a. grade were commercially available and used without further purification.

A mixture of As_2O_5 (0.0459 g, 0.2 mmol), $Na_2MoO_4\cdot 2H_2O$ (0.0968 g, 0.4 mmol), 2-aminopyridine (0.0941 g, 1 mmol), and H_2O (15 mL) was sealed in a 25 mL Teflon-lined bomb and heated at 170 °C for 120 h, then slowly cooled to r. t. Henna block-like crystals were collected by fil-

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Table 1. Crystal and refinement data for compound **1**.

Formula	$C_{100}H_{80}As_4Mo_{48}N_{40}O_{166}$
M_r	9402.84
Crystal size, mm^3	0.20 × 0.18 × 0.18
Crystal system	monoclinic
Space group	$P2_1/n$
a, Å	13.310(3)
b, Å	22.399(5)
c, Å	19.820(4)
β, deg	99.99(3)
V, Å^3	5819(2)
Z	1
D_{calcd}, g cm^{-3}	2.68
$\mu(MoK_\alpha)$, cm^{-1}	3.2
$F(000)$, e	4436
hkl range	$-15 \rightarrow 11$, ±26, ±23
Refl. measured / unique / R_{int}	42184 / 10259 / 0.0445
Param. refined	934
$R(F)$ / $wR(F^2)$[a] (all refls.)	0.0534 / 0.1384
A / B values for weighting scheme[b]	0.0634 / 59.9821
GoF (F^2)[c]	1.093
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	1.67 / −1.15

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$;
[b] $w = [\sigma^2(F_o{}^2)+(AP)^2+BP]^{-1}$, where $P = (\mathrm{Max}(F_o{}^2, 0)+2F_c{}^2)/3$;
[c] $\mathrm{GoF} = [\Sigma w(F_o{}^2 - F_c{}^2)^2/(n_{obs} - n_{param})]^{1/2}$.

Table 2. Selected interatomic distances (Å) and angles (deg) for compound **1**.

Mo(1)-O(3)	1.665(4)	Mo(1)-O(2)	1.947(4)
Mo(1)-O(1)	1.872(4)	Mo(1)-O(4)	1.959(4)
Mo(1)-O(5)	1.881(3)	Mo(1)-O(38)	2.344(3)
As(1)-O(39)	1.659(3)	As(1)-O(37)	1.662(3)
As(1)-O(38)	1.660(3)	As(1)-O(36)	1.668(3)
O(3)-Mo(1)-O(1)	101.22(18)	O(1)-Mo(1)-O(4)	156.30(15)
O(3)-Mo(1)-O(5)	102.20(17)	O(5)-Mo(1)-O(4)	83.96(15)
O(1)-Mo(1)-O(5)	92.54(16)	O(2)-Mo(1)-O(4)	85.48(15)
O(3)-Mo(1)-O(2)	100.68(17)	O(3)-Mo(1)-O(38)	170.79(16)
O(1)-Mo(1)-O(2)	88.70(16)	O(1)-Mo(1)-O(38)	73.00(13)
O(5)-Mo(1)-O(2)	156.38(15)	O(5)-Mo(1)-O(38)	85.41(13)
O(3)-Mo(1)-O(4)	102.43(18)	O(2)-Mo(1)-O(38)	72.40(13)
O(39)-As(1)-O(38)	109.59(16)	As(1)-O(36)-Mo(7)	123.15(16)
O(39)-As(1)-O(37)	109.57(16)	As(1)-O(36)-Mo(11)	123.81(18)
O(38)-As(1)-O(37)	109.59(15)	Mo(7)-O(36)-Mo(11)	92.36(11)
O(39)-As(1)-O(36)	109.09(15)	As(1)-O(36)-Mo(8)	123.55(16)
O(38)-As(1)-O(36)	109.58(16)	Mo(7)-O(36)-Mo(8)	93.25(12)
O(37)-As(1)-O(36)	109.41(16)	Mo(11)-O(36)-Mo(8)	91.77(11)
Mo(8)-O(26)-Mo(5)	153.1(2)	Mo(6)-O(30)-Mo(8)	151.2(2)
Mo(5)-O(27)-Mo(6)	151.6(2)	Mo(12)-O(31)-Mo(6)	122.15(18)
Mo(8)-O(29)-Mo(11)	122.03(18)	Mo(12)-O(33)-Mo(9)	151.5(2)

tration, washed with distilled water, and air-dried to give a yield of 55 % for **1** based on the initial $Na_2MoO_4\cdot 2H_2O$ input. Anal. for compound **1**: calcd. C 12.69, H 1.55, N 5.92, Mo 48.64, As 3.16; found C 12.74, H 1.52, N 5.94, Mo 48.68, As 3.13.

X-Ray crystallography

The reflection intensities of compound **1** were collected at T = 113(2) K using a Rigaku Saturn CCD area detector single-crystal diffractometer with confocally monochromatized MoK_α radiation (λ = 0.71073 Å), using ω scans. An absorption correction was applied using the program CRYSTALCLEAR [15]. The structure was solved with Direct Methods using SHELXS-97 [16] and refined by full-matrix least-squares on F^2 with SHELXL-97 [17]. All hydrogen atoms were generated geometrically. All non-hydrogen atoms were finally refined with anisotropic displacement parameters, hydrogen atoms with isotropic displacement parameters. Further information about the crystal data and structure determination is summarized in Table 1. Selected interatomic distances and bond angles are given in Table 2.

CCDC-777256 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Catalytic reaction for acetone elimination

The catalytic performance of compound **1** was measured in a continuous-flow fixed-bed micro-reactor filled with 0.15 g of compound **1**. The simulacrum of polluted air was prepared by bubbling clean air into a container filled with an acetone solution, and then diluting the gas with clean dry air. The initial acetone concentration of the reaction gas was controlled by changing the proportion of the bubbling gas and the diluent gas. The reactant mixture was fed to the tube reactor at a flow rate of 2.5 mL min^{-1}.

The reaction temperature was raised from room temperature to a certain temperature at which acetone was not longer detected in the effluent gases. The concentration of organic compounds of the effluent gases was analyzed on-line by a gas chromatograph GC-9800, equipped with a packed column with Porapak-Q and flame ionization detector (FID). Blank experiments were carried out in the absence of compound **1**.

Results and Discussion

Crystal and molecular structure

Compound **1** consists of a discrete Keggin-type $[AsMo_{12}O_{40}]^{3-}$ polyoxoanion, $[C_5H_7N_2]^+$ cations, $C_5H_6N_2$ molecules, and water molecules (Fig. 1). The Keggin-type polyoxoanion $[AsMo_{12}O_{40}]^{3-}$ is made up of a central AsO_4 tetrahedron surrounded by twelve MoO_6 octahedra present in four Mo_3O_{13} groups. The central AsO_4 tetrahedron shares its oxygen atoms with four Mo_3O_{13} groups, each of which is made up of three edge-sharing MoO_6 octahedra. The Mo_3O_{13} subunits are joined to each other by a corner-sharing mode. Each of the Mo atoms in the octahedral en-

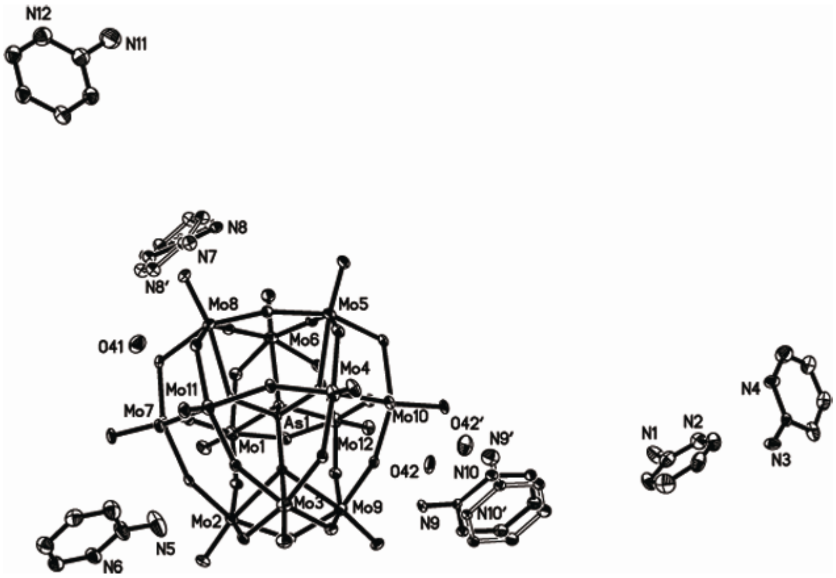

Fig. 1. ORTEP view of the structure of compound **1** in the solid state with atom numbering.

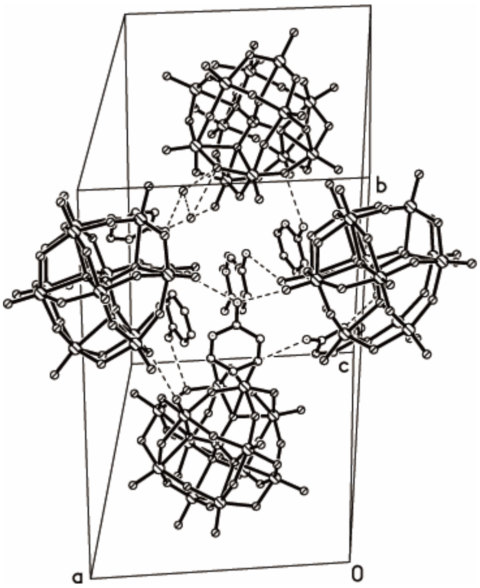

Fig. 2. The 2D structure of compound **1** built up through intermolecular hydrogen-bonding interactions.

vironment connects with one terminal oxygen atom (O_t), four doubly bridging oxygen atoms (O_b), and one triply bridging oxygen atom(O_c), which form a distorted MoO_6 octahedron. The Mo–O_t distances are in the range of 1.656(4) – 1.685(4) Å, the Mo–O_b distances of 1.851(4) – 1.985(4) Å, and the Mo–O_c distances of 2.332(3) – 2.358(3) Å. The alternating short and long Mo–O_b–Mo bonds lead to Mo atoms being slightly shifted off the mirror planes of the Mo_3 triangle in the Keggin anions [18]. The As–O distances are in the range of 1.659(3) – 1.668(3) Å, while the O–As–O angles vary from 109.09(15) to 109.59(16)°, compatible with those of the corresponding $[Mo_{12}AsO_{40}]$ group in $[\{Cu_3(qtpyr)_2\}Mo_{12}AsO_{40}]\cdot 0.4H_2O$ [13]. In the title compound, $[C_5H_7N_2]^+$ cations, $C_5H_6N_2$ molecules, H_2O molecules and polyoxoanions are connected through electrostatic interactions and strong intermolecular hydrogen bonds. In the unit cell, the polyoxoanions, 2-aminopyridine and water molecules are alternatively arranged well ordered along the crystallographic *a* axis, while the water and 2-aminopyridine molecules occupy cavities in the polyoxometalate structure (Fig. 2).

IR and UV/Vis spectra

The infrared spectra of compound **1** before and after the catalytic reaction were tested. These IR spectra showed strong absorption bands located at 1661, 1621, 1541, and 1473 cm^{-1} which may be assigned to phenyl group C-N and C-C stretching vibrations. The absorptions at 953, 888, 843, and 761 cm^{-1} can be assigned to ν(As-O) and ν(Mo-O) stretching vibrations of the $[AsMo_{12}O_{40}]^{3-}$ polyoxoanions [19], the characteristic pattern of absorption bands of a Keggin structure. IR spectra before and after the catalytic reaction did not change, indicating that the compound remains unchanged in the catalytic reaction.

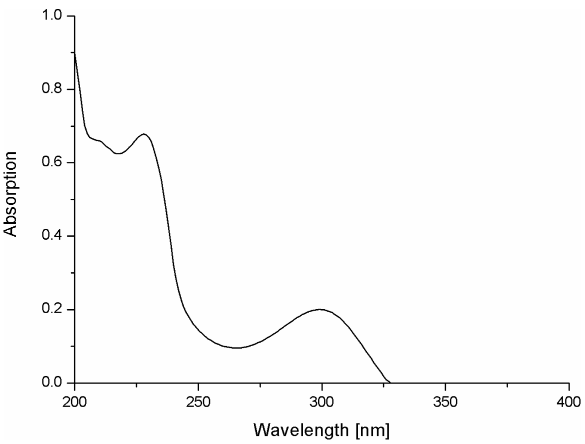

Fig. 3. UV/Vis spectrum of compound **1**.

The UV/Vis spectrum of a 1 M H_2SO_4 aqueous solution of **1** at r. t. is depicted in Fig. 3.

The strong oxygen-to-metal charge transfer (LMCT) absorption maxima occur at 211 and 228 nm, which can be assigned to the $O\rightarrow Mo_d$ LMCT and $O\rightarrow Mo_{b/c}$ LMCT of $[AsMo_{12}O_{40}]^{3-}$, respectively [20]. The weak absorption peak at 301 nm may indicate charge-transfer interactions between organic cations and polyoxoanions [21].

TG-DTA analysis

The TG-DTA analysis of compound **1** was performed in the temperature range of 50 – 706 °C. The first endothermic peak at 178 °C corresponds to a loss of crystal 2-aminopyridine and water molecules, the weight loss of this step being 9.5 %, in accordance with the calculated value (9.3 %). From 388 to 700 °C, there are two exothermic peaks at 469 and 491 °C. The TG curve exhibits a weight loss corresponding to the release of 2-aminopyridinium cations and the decomposition of $[AsMo_{12}O_{40}]^{3-}$ polyoxoanions. The weight loss of this step is 17.2 %, in accordance with the calculated value (17.8 %).The final residue is asssumed to be MoO_3.

Catalytic reaction

Blank experiments showed that the acetone in a simulacrum of polluted air was hardly eliminated without compound **1** as a catalyst. The catalytic performance measurement results have shown that the acetone of concentration 5.3 g m^{-3} provided at a flow rate of 2.5 mL min^{-1} was completely eliminated at 150 °C over 0.15 g of compound **1** as catalyst. Compound **1** thus has a better catalytic oxidation activity for eliminating acetone at lower temperature, classifying it is a potential material for catalytic elimination of VOCs.

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